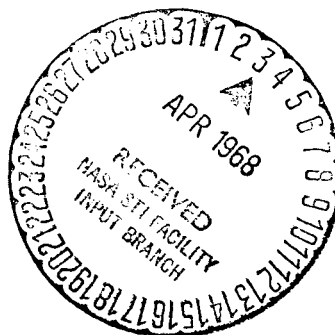


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OXYGEN IN SILICON

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ABSTRACT: Survey of current methods for determining the oxygen concentration in silicon semiconductors. Various properties of oxygen are discussed in view of the lack of electrical effects in oxygen impurities. The formation of compounds exhibiting donor properties at certain temperatures during heat treating is considered, together with the effects of oxygen on carrier lifetime, surface etching, and dislocations. A method involving the measurement of absorption in the $9.1\text{-}\mu$ range to determine oxygen content is described in detail.

Oxygen in Silicon

Admixtures in semiconductors can, on the basis of their effect on electric conductivity, be divided into electrically active and electrically inactive ones. The former make a contribution to electric conductivity, and may be detected by measuring the specific resistance and the Hall effect. Present as admixtures of this type in germanium and silicon are Al, B, In, P, Sb, As and Bi, as well as Si, Fe, Cu, Zn, Au, etc. Admixtures of the second category do not make a contribution to electric conductivity, and therefore their concentration cannot be determined on the basis of change of the electrical properties of the semiconductor. In silicon, an obligatory admixture of the second category is oxygen. /* 118

When a silicon monocrystal is grown according to the Chekhral'skiy method, oxygen gets into the fusion when the walls of the quartz crucible become dissolved. The oxygen content in such monocrystals usually reaches $10^{17} - 10^{18} \text{ cm}^{-3}$. If the monocrystal is being grown by the crucibleless zonal melting method, oxygen enters the fusion from the gaseous phase. In the case of a helium atmosphere the fusion already contains a considerable amount of oxygen when its partial pressure is 0.1 mm Hg. A mixture of 10% oxygen and 90% helium behaves like a pure oxygen atmosphere [1]. In case of melting in a hydrogen atmosphere, oxygen gets into the monocrystal due to the presence of insignificant quantities of water vapor in the hydrogen stream. Thus, in any case oxygen is an obligatory admixture in silicon monocrystals.

As has already been indicated above, oxygen is an electrically neutral admixture. Atomically distributed oxygen does not affect the specific conductance (σ) and the carrier mobility (μ) in silicon. However, if silicon monocrystals containing oxygen are subjected to heat treatment at $450 - 500^\circ\text{C}$, intensive formation of thermodonors will take place [2 - 9]; the concentration of these depends strongly upon temperature, and exponentially approaches a certain maximum. Here the value of the maximum decreases as the temperature rises, but it is attained much more rapidly. Below 430° the maximum is not attained even after 500 hours of treatment. /119

* Numbers in the margin indicate pagination in the foreign text.

The process of thermodonor formation is most efficient at 450° (up to $5 \times 10^{16} \text{ cm}^{-3}$). With a further increase in temperature the amount of thermodonors begins to decrease exponentially, and their number tends toward a new limit value which exceeds the initial one. The time constant of the exponential decrease of the thermodonors is greater than the time constant of the exponential growth of their number. At a temperature of 1100°C the thermodonors are burnt out within several minutes. After treatment at 1100°C, there are no thermodonors in the material. If a specimen is held at 1100 - 1200°C for about 20 hours, the material becomes stabilized. An additional hour's treatment at 1300 - 1350°C eliminates the stabilization.

The described phenomena are connected with the presence of oxygen in silicon; this is indicated by the following factors.

1. They are observed only in specimens containing O_2 in perceptible quantities.
2. The distribution of thermodonors in the specimen is in good agreement with the distribution of oxygen in it.
3. The initial rate of formation of thermodonors is proportional to the fourth power of the oxygen concentration, and the maximum quantity of thermodonors is proportional to the third power of the oxygen concentration.
4. The decrease in the time of attaining the maximum quantity of thermodonors depends on increasing the oxygen content in the specimens.

It is assumed that in the heat-treatment process, SiO_4 complexes are formed at 400 - 500°C which possess the properties of donors, at 1000 - 1100°C precipitation of oxygen takes place in the form of SiO_2 complexes, and at 1300 - 1350°C the oxygen is again dissolved in the silicon lattice.

There exist data which indicate that when the oxygen concentration in a monocrystalline silicon rod is increased, the lifetime of the free carriers increases sharply [10 - 13]. This may be explained by the presence of recombination centers x in the monocrystal, which are deactivated upon interaction with oxygen. Such centers can be admixed atoms, dislocations, and defects of the "vacancy - interstice" type.

In n-type silicon specimens containing a considerable quantity of oxygen, /120
adhesion of the charge carriers has been detected which originates approximately at room temperature, increases as the temperature rises, and vanishes at a temperature of $\approx 200^\circ\text{C}$ [5]. Adhesion was not observed in specimens grown with a low rate of rotation; it could be increased or eliminated by means of appropriate heat treatment to change the state of the oxygen in the silicon. It has been established [5] that adhesion takes place by capture of the charge carriers onto an acceptor level with a depth of 0.38 eV from the bottom of the conductivity zone.

Oxygen is also said to affect the character of corrosion of the silicon surface [14 - 16], since an increase of the oxygen content in the crystal decreases the rate of corrosion. Thus, if a crystal obtained by zone melting is subjected to an hour's heat treatment at 1300°C in an oxygen atmosphere, the number of corrosion pits is less than that obtained after analogous processing in a vacuum. This effect makes it possible to observe oxygen diffusion.

It is presumed that oxygen atoms strive to pass into dislocation zones. To verify this, silicon specimens were annealed at 1000°C [17]. In the course thereof, there was a decrease in the area of the absorption peak of infrared radiation with a wavelength of 9.1 microns, which characterizes the concentration of optically active oxygen. For specimens with a high dislocation density (10^7 cm^{-2}), the decrease of the peak takes place more rapidly than for crystals with a lower (10^4 cm^{-2}) dislocation density. Thus, annealing stimulates the transition of oxygen atoms into an optically inactive state all the more strongly, the greater the number of dislocations in the crystal. It is natural to assume that the oxygen atoms "are precipitated" at the dislocations, thus disrupting part of those Si-O chemical bonds which determine the absorption peak at 9.1 microns.

Mention should also be made of the interaction of oxygen in silicon with elements of the third group of the periodic system: Al, Ga, B, etc. In particular, the authors of [18] have discovered that the interaction of O_2 with Al results in the formation of complexes which possess the properties of donors.

Because of this activity of oxygen, the precise quantitative analysis of oxygen in silicon acquires great importance. At present, several methods have been developed for determining the concentrations of electrically inactive admixtures in semiconductors: gas vacuum analysis, infrared absorption, the radioactive-isotope method, and the mass-spectrometry method. The method of oxygen analysis in silicon by means of absorption measurement in the 9.1 micron region [19] is in very extensive use. /121

Starting with 1.2 microns, silicon is transparent in the infrared region. In the 9.1 micron region, a sharp maximum appears on the absorption curve of infrared radiation.

For a long time it was impossible to establish precisely the nature of this absorption, until an entire series of facts convincingly demonstrated that in this case admixture absorption takes place, which is connected with the presence of oxygen in the silicon lattice. Kaiser [19] has proposed the following model for dissolving oxygen in the silicon lattice. Oxygen disrupts the bond between two silicon atoms with the formation of an isosceles triangle, the vertices of which are Si, Si, O. Absorption in the 9.1 micron region is explained by resonant absorption of the deformed Si-O bond.

The correctness of the model is confirmed by experimental data. Khrostevskiy [20], using the isotope O^{18} for his research, discovered an isotopic shift of the absorption band; the ratio of the oscillation intensities $\text{O} - \text{O}^{16}$ and $\text{O} - \text{O}^{18}$ also testifies in favor of the proposed model. The area of the absorption peak turned out to be directly proportional to the concentration of oxygen in the silicon (Fig. 1). For N independent Si-O oscillators the area of the absorption peak is described by the equation

$$\int \alpha_\nu d(h\nu) = kN, \quad (1)$$

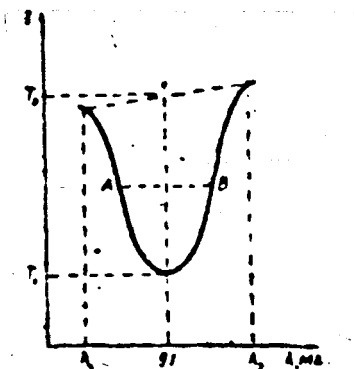


Figure 1

Since we are considering a very narrow frequency interval, the integral can be approximately replaced by the product

$$\sigma_{\max} H = kN; \quad (2)$$

here σ_{\max} is the absorption factor in the band maximum;

H is the half-width of the band,

i. e., the peak is approximated by a triangle. The absorption factor is found on the basis of the specimen transparency by the formula

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$$T = \frac{I}{I_0} = \frac{(1-R)^2 e^{-\sigma d}}{1-R^2 e^{-2\sigma d}}, \quad (3)$$

where R is the reflection factor of the specimen (for silicon in the region of 9.1 microns $R = 0.3$);

I_0 is the intensity of light falling on the specimen;

I is the intensity of light which passes through the specimen.

This method is suitable for determining an oxygen concentration upwards of $2 \times 10^{16} \text{ cm}^{-3}$.

An oxygen concentration $< 2 \times 10^{15}$ [sic] is found by the method of precipitating lithium from a supersaturated solution [21 -24]. The method is based upon the ability of lithium to form LiO^+ donor complexes with oxygen. This phenomenon was first discovered by Pell [23].

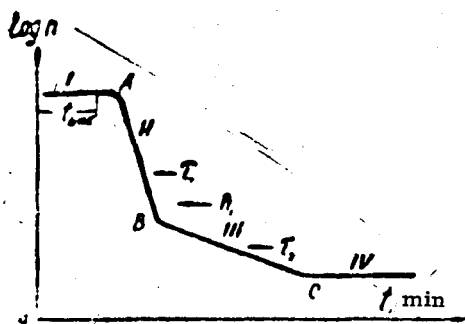
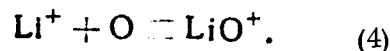


Figure 2

Donor complexes are formed as a result of the reaction



The oxygen is fully bound into complexes only with the presence of excess lithium and in the case of elevated temperature (the solubility of lithium increases). During chilling from high temperature to room temperature, the process of lithium precipitation continues until an equilibrium between the LiO^+ complexes and the dissolved oxygen is attained. Since each

dissolved atom contributes one electron to the conductivity zone, the precipitation may be studied on the basis of the change of electric conductivity. The kinetics of the precipitation of lithium from a supersaturated solution is shown in Fig. 2; the logarithm of the concentration of the current carriers is plotted along the ordinate, the time of precipitation is plotted along the abscissa.

Sector I corresponds to an incubation period, during which apparently the nuclei or precipitation centers are formed. In sector II (AB) the excess lithium is rapidly precipitated. Point B corresponds to the moment when all of the excess lithium has been precipitated, and the equilibrium of reaction (4) shifts to the left. The disruption of the LiO^+ complexes is accompanied by further precipitation of lithium, and equilibrium is established in point C of sector III. Thus, by determining the concentration of current carriers in point B, it is possible to measure the concentration of LiO^+ complexes and, consequently, the oxygen concentration.

Recently Nozaki, Simada [26, 27] [sic] have proposed a radioactivation analysis of oxygen in silicon. Silicon specimens are exposed in a cyclotron to σ particles O^{16} (σ , pn) F^{18} . The oxygen interacts with the σ particles and is converted into radioactive F. A conclusion concerning the concentration of oxygen in the irradiated specimen is arrived at on the basis of the quantity of radioactive fluorine. However, the radioactivation analysis is very complicated in the technological sense.

Information is available [28] [sic] that the concentration of oxygen in silicon can be evaluated on the basis of the photoconductivity spectra of extremely pure monocrystals of p-type silicon before and after irradiation by electron flows with a power of about 1 MeV.

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